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FACILE SYNTHESIS OF N, N-DIMETHYL PARAPHENYLENE DIAMINE DIHYDROCHLORIDE: A PHOTOGRAPHIC DEVELOPER DYE

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ABSTRACT

A Facile route has been developed to afford N,N- Dimethyl para phenylene diamine dihydrochloride (NNPPDA) under high pressure condition using N,N-Dimethyl amine HCl and 4-Chloro Nitrobenzene in DMF/$NaHCO_3$ system followed by Raney nickel reduction and hydrochloride salt formation. This scalable and economical process ends up with 99% isolated yield on kilo scale.

Key words: N, N Dimethyl Para Phenylene Diamine, 4-chloro Nitrobenzene and N, N-Dimethyl amine HCl.

INTRODUCTION

N,N-Dimethyl para phenylene diamine dihydrochloride (NNPPDA) is very important dye intermediate in developing photographic images[1], in evaluation of oxidative status of human plasma[2], in synthesis of p-dimethylamino benzene diazo sodium sulfonate[3] (DEXON fungicide), in analyzing low level of peroxy acetic acid[4] in water and synthesis of Methylene Blue. The reported classical route for lab scale was halogen replacement (SN_2Ar reaction) of 4-nitro-chlorobenzene using N, N-dimethylamine HCl in pyridine/$NaHCO_3$ system[5] followed by Bechamp type reduction and hydrochloride salt formation. The process was time consuming and was not scalable due to pyridine handling (causing impotency).

Another route was halo replacement of above mentioned key raw material in DMF/$CuSO_4$ system and Ethanol/ $NaHCO_3$ system[6] as well at their refluxing temperature respectively which ended with low yield and failed to scale up at kilo level. As per dye chemistry approach, the well known route followed was nitrosation, reduction with Zn/Fe/$SnCl_2$, high vacuum distillation and hydrochloride salt formation. The process ended up with 50% yield leaving behind large amount of inorganic waste.

To improve the yield and overcome the problems faced in scaling up, we developed a process which can be scaled up to several kilograms to achieve excellent yield using 4-chloro nitro benzene in DMF/$NaHCO_3$ system under pressure (@25kg/cm^2) at 120°C temperature for 2 hr, followed by reduction using Raney Nickel and hydrochloride salt formation. This process is less time consuming with optimum yield of 99% of final molecule (NNPPDA).

As per the collision theory, in order for the reaction to occur, the particles or the molecules should colloid each other. In the 1st and 2nd references the reaction of halo replacement are performed at 1atm pressure, were the collision rate of molecule is less so the rate of reaction is slow and takes longer time(figure-1a), which affects the energy cost. When the same reaction is performed at higher pressure, the collision rate increases drastically, this accelerates the reaction (figure-1b). Also the collision theory also states that increasing the temperature (only one parameter) can increase the rate of collision, but the major problem while scaling up the reaction is loss of N, N-dimethyl amine which leads to extra consumption of raw material. So we performed the reaction in closed condition were one more parameter i.e. pressure was added and optimization and robustness of the process was studied. This gave us a good advantage with cost effectiveness, less time consumption for halo replacement step.

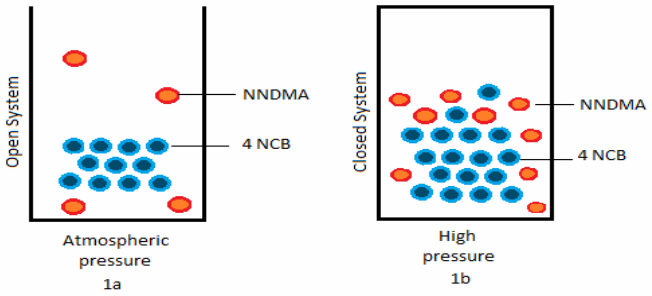


Fig.-1: Comparison of collision rate in open system and closed system

In nitro to amine reduction step, classical route like Bechamp reduction, Wolfkishner type reduction, nitroso to amine reduction using Zn/Fe/$SnCl_2$ was followed. This type of reductions ends up with large amount of non disposable inorganic sludge. We altered this step by giving touch of green chemistry approach using Raney Nickel under 5 Kg hydrogen pressure, ending up with "No waste" and 80% catalyst recovery and reusability.

EXPERIMENTAL

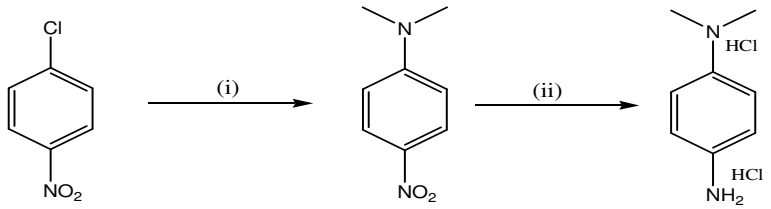
All the chemicals were purchased from Loba Chemie with minimum purity > 99%. Melting point, HPLC and IR values recorded by Veegomatic, Waters and Thermo scientific respectively. Reactions were carried out in S.S high pressure reactor (Nano- mag make).

N, N –Dimethyl-4-Nitro Aniline

500.0g (3.17mol) 4-chloro-nitro-benzene, 2.0 lt. dimethyl formamide, 466.0g (5.71mole) N, N dimethyl amine hydrochloride (NNDMA.HCl), 740.0g (8.8mol) sodium bicarbonate and water was charged into 5 ltr capacity S.S pressure reactor. The reaction was heated to 120°C at 500 RPM for 2 hrs. There was steady increase in pressure from 1kg to 20kg/cm^2. After completion of reaction (monitored by TLC), reaction was cooled by internal cooling coil. The slurry was quenched in water and filtered. Wet cake was washed with water. On drying in tray drier, 522.0g (99.0 % yields) was obtained with 99% HPLC purity. m.p 164°C (lit m.p163-166 °C); IR (KBr, cm^{-1}):3088(NH), 1600(NH-bend), 1583, 1383, 1310(NH stretch).

N, N-Dimethyl-1, 4-phenylenediamine.2HCl

500.0g (3.0mol) N, N-dimethyl -4-nitro-aniline, 50.0g Raney nickel, and 2.5ltr ethanol was charged into 5ltr capacity S.S pressure reactor. Nitrogen was flushed 2 times at 1kg/cm^2 and hydrogen was flushed at 1 kg/cm^2. The reactor was pressurized with hydrogen at 5 kg/cm^2 and was maintained at the above pressure for 2 hr at 45°C. After completion of reaction (monitored by TLC), the catalyst was filtered off and the filtrate was charged into a reaction vessel.



Reagents and conditions: (i) DMF, $NaHCO_3$, NNDMA. HCl 120°C, 2hrs (ii) Raney Ni, Ethanol, H_2 pressure 5kg/cm^2, IPA. HCl 2hrs

Scheme-1: Proposed Synthetic route

The pH of filtrate was adjusted to acidic side i.e. pH 1-2 by IPA.HCl. After maintaining the reaction for 1 hr, the slurry was filtered and washed with 200.0mL ethanol. On drying in vacuum tray drier, 622.0g (99.0% yield) was obtained with 99% HPLC purity. m.p 213°C (lit m.p 210-215 °C); IR (KBr, cm^{-1}): 3099, 3025, 3012(NH_2.stretch) 1570, 1504, 1475(NH-stretch).

RESULTS AND DISCUSSION

We studied the effect of temperature and pressure on the rate of reaction, to produce N, N –Dimethyl-4-Nitro Aniline. Improvisation in the rate of reaction was observed when the temperature of the reaction mass was increased from 80°C to 120°C, correspondingly increase in pressure was observed from10 kg/cm^2 to20 kg/cm^2 (Table-1) regardless to the isolated yield. We observed direct proportionality between temperature, pressure and the rate of reaction, and found the optimum variables to reduce the time and additional raw NNDMA.HCl consumption.

Table-1: Effect of temperature and pressure on the rate of reaction

Entry	Temperature(°C)	Pressure(kg/cm^2)	Time(hr)	Yield
1	80	10	10.5	99%
2	90	12	8.5	99%
3	100	15	6.3	99%
4	110	18	4.0	99%
5	120	20	2.0	99%
All the reactions were carried out in 5 lit capacity high pressure reactors with same input.				

The effect of raney nickel catalyst loading was also investigated for the reduction of N, N –Dimethyl-4-Nitro Aniline to N, N-Dimethyl-1,4-phenylenediamine. We observed no impact of catalyst loading on the yield, but there was change in rate of reaction. When the catalyst loading was minimum (1%) the time required for the completion of the reaction was approximately 10.5 hr i.e. higher catalyst loading increased the rate of reaction. By reducing the time period less energy was consumed (Table-2).

Table-2: Effect of catalyst loading on rate of reaction

Entry	Amount of Raney Nickel (%)	Pressure(kg/cm^2)	Temperature(°C)	Time(hr)
1	1	5	45	10.5
2	2	5	45	8.5
3	3	5	45	6.3
4	4	5	45	4.0
5	5	5	45	2.0
All the reactions were carried out in 5 lit capacity high pressure reactor with same input				

CONCLUSION

A new scalable route has been developed for the preparation of N, N-Dimethyl para phenylenediamine.2HCl.

ACKNOWLEDGEMENTS

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